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CITATION:

TANAKA, Norifumi ...[et al]. <Preliminary>Effect of Oxalic Acid on the Oxidative Breakdown of Cellulose by the Fenton Reaction. Wood research : bulletin of the Wood Research Institute Kyoto University 1994, 81: 8-10

ISSUE DATE:

1994-09-30

URL:

http://hdl.handle.net/2433/53252

Preliminary

Effect of Oxalic Acid on the Oxidative Breakdown of Cellulose by the Fenton Reaction*[1]

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(Received June 1, 1994)

Keywords: Oxalic acid, Fenton oxidation, cellulose, viscosity, brown-rot decay.

The drastic decrease in viscosity of cellulose at the incipient step of brown-rot wood decay process was first reported by Cowling[1] and later by Ishihara[2]. The rapid decreases in mechanical strengths observed during the brown-rot decay[3] have been ascribed to the rapid breakdown of cellulose in wood.

Halliwell first observed that cellulose is rapidly depolymerized by the Fenton oxidation ($Fe^{2+}+H_2O_2 \rightarrow Fe^{3+}+HO^-+HO\cdot$)[4]. Koenigs reproduced a similar depolymerization of cellulose in wood which had been treated with the Fenton reaction and proposed that brown-rot fungi attack wood with Fenton type oxidation at an earlier step[5]. Schmidt et al. proposed that oxalic acid plays a key role in reduction of Fe^{3+} to Fe^{2+}, which increased the cellulolytic activity (cellulose$\rightarrow CO_2$) of the iron-H_2O_2 non-enzymatic decay system[6]. However, the higher concentration of oxalic acid inhibited the Fenton reaction; almost conplete inhibition was observed when oxalate/Fe ratio=10 at 1 mM Fe[6]. Recently, Barr et al. have also reported that oxalate scavenges OH radical produced in a lignin peroxidase system[7].

Alternatively, the cellulose chain was first demonstrated to be hydrolytically broken down by a dilute oxalic acid solution[8]. We have reported a possible participation of acid hydrolysis in the faster degradation of cellulose during brown-rot decay since brown-rotters secrete significant amounts of oxalic acid, thereby lowering the pH in the medium[9]. Recently, Green III et al. have also reported a significant effect of the acid on the breakdown of cotton cellulose[10,11].

We report here the effects of various organic acids as physiological metabolites on the hydrolytic and oxidative depolymerization of pulp cellulose. Table 1 shows decreases in viscosity of the cellulose samples which were separately treated with 1% acetic, formic,

*[1] A part of this work was presented at the 43rd Annual Meeting of the Japan Wood Research Society in Morioka, Aug. 1993.

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Table 1. Changes in viscosity of pulp cellulose after treatment with various organic acids for 4 weeks at 33°C.

Organic acid used	(pH)	Viscosity (cP)	(%)
Control	(5.6)	29.6	(100)
Acetic acid	(2.8)	26.8	(91)
Formic acid	(2.2)	27.0	(91)
Malic acid	(2.4)	27.4	(93)
Citric acid	(2.3)	27.3	(92)
Oxalic acid	(1.3)	22.0	(75)

Note: Coniferous wood pulp (20 g) each was aseptically incubated in 1% organic acid solution at 33°C for 4 weeks and viscosities of the recoverd pulp samples were measured by the Tappi standard method with cupriethylenediamine hydroxide (TAPPI T230 om-82).

malic, citric, and oxalic acid solutions. The results clearly indicate that oxalic acid is the strongest for depolymerization of cellulose among the organic acids tested, although depolymerization speed is not as fast as that observed with the Fenton degradation (Fig. 1).

Fig. 1 shows viscosities of the pulp which was treated with the Fenton type oxidation in

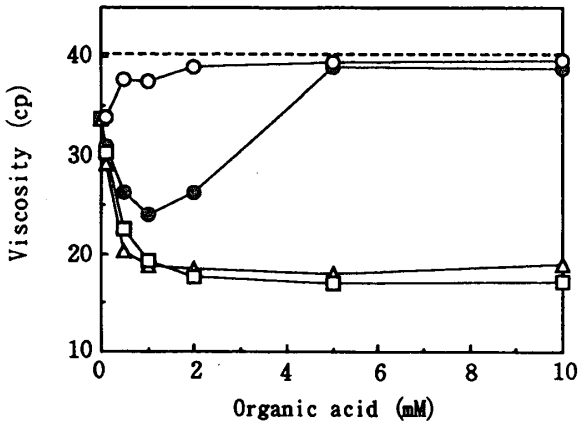

Fig. 1. Effects of various organic acids on changes in viscosity of cellulose during the Fenton type oxidation. Note: The reaction mixture (40 ml of distilled water) contained 1 g of beech pulp (Kappa value; 16.8), 1.5 mM of H_2O_2 added, ferric chloride (0.1 mM), and each organic acid (0.1, 0.5, 1.0, 2.0, 5.0, and 10 mM). The Fenton oxidation was initiated by the addition of H_2O_2 solution and the mixture was incubated for 24 hrs at 30°C with occasional stirring. The cellulose samples were recovered, washed with distilled water, and treated with $NaBH_4$ (50 mg in 33 ml of water). After drying the treated pulps (250 mg dry wt. each) were dissolved in the cupriethylenediamine hydroxide solution and the viscosities were measured by the TAPPI standard method (TAPPI T230 om-82).

the presence of varying amounts of each organic acid in the reaction mixtures. The results indicate that although a control system (no addition of an organic acid) reduced the viscosity significantly (to 85% of the original value), the organic acids affected the degradation of cellulose by the Fenton oxidation in different ways as follows: a) Citric acid inhibited the decrease in viscosity with an increase in concentrations of the acid. b) Both acetic and succinic acids accelerated the degradation of cellulose. c) Oxalic acid most effectively accelerated the degradation around the region of 1 mM concetration, whereas it begins to significantly inhibit the degradation at the 3 mM concentration, causing a complete inhibition over the range of 5 mM of oxalic acid.

The maximal decrease in viscosity, or about 60% of the original value, was observed at 1 mM oxalic acid (oxalate/Fe=10), whereas at 5 mM oxalic acid (oxalate/Fe ratio=50) no decrease in the viscosity was observed. The present results indicate that if the oxalate/Fe ratio exceeds 50, the Fenton oxidation is inhibited, which is consistent with the previous findings[6,7]. Alternatively, we observed that the reduction of Fe^{3+} to Fe^{2+} by oxalate is not prerequiste for causing the Fenton reaction, as can be seen in the control sytem without oxalate added (Fig. 1). However, since the oxalic acid-mediated hydrolysis of cellulose (Table 1) is a very slow step, it is also important to investigate the breakdown of hemicellulose and lignin carbohydrate complex during the brown-rot wood decay process to account for the rapid loss of the mechanical strengths of brown-rotting wood. Thus, the amount of oxalic acid produced in the decaying wood may control the oxidative degradation of wood components in either a positive or negative way.

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